EDGEWOOD CHEMICAL BIOLOGICAL CENTER

U.S. ARMY RESEARCH, DEVELOPMENT AND ENGINEERING COMMAND
Aberdeen Proving Ground, MD 21010-5424

ECBC-CR-125

OPTIMIZATION AND VALIDATION OF A SURFACE WIPE METHOD TO DETERMINE CYANIDE AND CYANATE: APPLICATION TO THE EMERGENCY DESTRUCTION SYSTEM

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Gunpowder, MD 21010-0068**

August 2012

U.S. ARMY RDECOM

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REPORT DOCUMENTATION PAGE

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
XX-08-2012	Final	Jun 2005 – Jul 2006

4. TITLE AND SUBTITLE	5a. CONTRACT NUMBER
Optimization and Validation of a Surface Wipe Method to Determine Cyanide and Cyanate: Application to the Emergency Destruction System	DAAD13-03-D-0017
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)	5d. PROJECT NUMBER
Morrissey, Kevin M.; Ruth, Jill L.; Fouse, Janet C.; Cheicante, Richard L.; and Flowers, Aaron K. (SAIC)	
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)	8. PERFORMING ORGANIZATION REPORT NUMBER
Science Applications International Corporation, P.O. Box 68, Gunpowder, MD 21010-0068	ECBC-CR-125

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S)
Director, ECBC, ATTN: RDCB-DRP-C, APG, MD 21010-5424	
	11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES

COR: Joseph D. Williams 410-436-4878

14. ABSTRACT-LIMIT 200 WORDS

The U.S. Army Product Manager for Non-Stockpile Chemical Materiel could deploy the Explosive Destruction System to neutralize materiel containing cyanide. A surface-sampling method was required to ensure operator safety and demonstrate the equipment was not contaminated. A surface wipe method for free cyanide and cyanate was successfully validated using collection protocols suitable for personnel wearing personal protective equipment in a contaminated environment. There were no significant differences in method performance for free cyanide or cyanate. Under the conditions evaluated, the overall average accuracy (spike recovery) values from the wipe material were 76.7%, with a 95% confidence interval of 75.7 to 77.6% and from a single wipe used on an impervious surface were 45.4 %, with a 95% confidence interval of 42.9 to 47.9%. The overall detection limits for the entire process was 0.13 mg free cyanide or 0.10 mg free cyanate per wipe. Validated collection, extraction, and analysis protocols are included in the report.

15. SUBJECT TERMS

EDS	Contamination	Free cyanide	Free cyanate	Total cyanide
AC	CK	Wipe method	Method validation	Demilitarization

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Renu B. Rastogi
					19b. TELEPHONE NUMBER *(include area code)*
U	U	U	UU	52	(410) 436-7545

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PREFACE

        The work described in this report was authorized under Contract No. DAAD13-03-0017. The work began in June 2005 and was completed in July 2006.

        The use of either trade or manufacturers' names in this report does not constitute an official endorsement of any commercial products. This report may not be cited for purposes of advertisement.

        This report has been approved for public release.

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1.   INTRODUCTION

1.1   Background

          The U.S. Army has the mission to provide centralized management and direction
to the Department of Defense (DoD) for the safe destruction of all U.S. non-stockpile chemical
materiel (NSCM) as defined in Public Law 102-484, 23 October 1992. Destruction of NSCM,
including recovered chemical warfare materiel (RCWM), will be in accordance with Federal
laws, policies, regulations, and directives, as well as applicable state and local laws and
regulations. The Army is the DoD focal point for the coordination of all matters relating to
NSCM destruction. This is accomplished by developing, constructing, fielding, and supporting
the necessary capabilities and materiel used to characterize, contain, transport, store, treat, and
dispose of NSCM for both routine and emergency response scenarios.

          RCWM consists of older chemical munitions that have been recovered outside the
controlled chemical stockpile. Historically, upon discovery of chemical warfare materiel
(CWM), explosive ordnance disposal technicians would identify and assess the condition of the
munition and determine whether the ordnance was filled with toxic chemicals and if it was safe
for transportation and storage. Chemical munitions that were determined to be safe were over-
packed (placed into a container with packing material as appropriate) and stored onsite or
transported by the 22nd Chemical Battalion (previously known as U.S. Army Technical Escort
Unit) to an appropriate chemical storage facility. Those RCWM items that could not be
transported or stored, due to unacceptable risks, were destroyed onsite using emergency
destruction procedures.

          The U.S. Army Product Manager for Non-Stockpile Chemical Materiel
(PMNSCM) is responsible for the destruction of several categories of chemical warfare materiel
in a safe, cost effective, environmentally sound manner, which is in compliance with the
Chemical Weapons Convention.[1] In April 2005, a partially filled cylinder of hydrogen cyanide
(AC or HCN, Chemical Abstract Service [CAS] no. 74-90-8) violently ruptured, causing
significant damage to a laboratory located at Aberdeen Proving Ground (APG), MD. The
subsequent accident investigation revealed there were seven additional cylinders of AC and one
cylinder of cyanogen chloride (CK or ClCN, CAS no. 506-77-4) also located at APG that were
likely to be unstable and should be destroyed.[2] To support this mission, PMNSCM deployed the
Explosive Destruction System (EDS) to treat these items.[3] During the EDS campaign, seven
cylinders of AC and one cylinder of CK, containing a total of 73 lb of fill materiel, were
successfully destroyed.[4] This report summarizes efforts to validate a surface wipe method to
collect and measure free cyanide and cyanate ions on surfaces of the EDS that could be
contaminated. Preliminary results from this effort were presented at the DoD-sponsored 2007
Chemical Materiel Agency's Monitoring, Environmental, Closure, and Quality Roundtable.[5]

1.2   Problem

Once the EDS campaign to demilitarize the AC and CK cylinders was completed, the EDS operators used glass fiber filters, moistened with deionized water, to wipe the EDS surfaces that had been in contact with the neutralent to collect "wipe samples" of any cyanide found on the surfaces. A total of 22 wipe samples were collected. The glass fiber filter was a 90 mm, Type GF-6, borosilicate glass filter manufactured by Whatman (now GE Healthcare Life Sciences, Pittsburgh, PA). Prior to collecting the wipe samples, no efforts had been conducted to demonstrate that this filter material was suitable for collecting free cyanide from impervious surfaces. The wipe samples were received in the laboratory and stored at ~4 °C until they were extracted with 0.01 wt% caustic solution. The extracts were analyzed by an established capillary electrophoresis (CE) method,[6,7] but the extraction process for these analytes had not been validated.

In all cases ($n = 22$), there was no free cyanide ion detected on any of the wipe samples. In addition, there was no cyanide ion detected in any ($n = 4$) of the laboratory wipe spikes. The laboratory matrix spikes were 342 µg of cyanide ion spiked onto a dry filter then extracted within 10 min of being spiked. The lack of recovery was thought to be because of oxidation of the cyanide ion to cyanate ion, but retrospective examination of the electropherograms did not reveal the presence of cyanate ion in any of the wipe samples. These results could not be used to support clearing of the EDS, since the "nondetects" (undetected cyanide results) could be false negatives due to the lack of recovery from the wipe material.

1.3   Study Objectives

The primary purpose of this effort was to optimize and validate an analytical protocol for the determination of free cyanide and cyanate ions from surfaces using a wipe method approach. The protocol had to be compatible with personnel wearing personal protective equipment (PPE) in a contaminated environment.

A secondary purpose of this effort was to identify potential areas where the method could be improved, and conduct experiments to evaluate the proposed improvements.

1.4   Literature Review

During a review of surface wipe methods published in 2007, the open literature through June 2006 was searched, and four references were cited that summarized work sampling chemical warfare agents (CWA) and toxic industrial chemicals (TICs) from surfaces using wipes.[8] In many cases, a woven polyester/cotton blend material was used as the wipe. In this literature review, no wipe methods were found that were used on surfaces to detect cyanide or cyanate in any form. Evaluation of the literature review led to the conclusion that there was no consensus on how to collect or analyze wipe samples, especially in relationship to CWA. In addition, details were lacking in most of the cited reports, including such basic information as what surface was used to demonstrate the method.

During a second review, the open literature along with government reports were searched from January 2006 through September 2008.[9] As a result of this second review, no methods were found for determining cyanide or cyanate on surfaces. In addition, many of the reviewed reports did not contain enough detail on how samples were collected or what surface(s) were utilized; therefore, the methods could not be validated or demonstrated. Although the two reviews did not provide a method specific enough for this task, they did provide a starting point for our initial efforts.

2.   EXPERIMENTAL PROCEDURES

This section describes the in-house experimental procedures and analytical methods used during this project. Included in this description are the incremental method development, optimization, and validation studies that were investigated to determine the suitability of a wipe method used to collect and measure residual free cyanide and cyanate ions.

2.1   Description of Wipe Material Candidates

There were 12 wipe material candidates evaluated during this effort. These wipes were constructed of materials that were consistent with suggestions contained in the literature found during the two reviews. The materials consisted of glass fiber with and without binders, filter paper, polymeric membranes, and gauze.[8,9] Descriptions and commercial sources of these wipe candidates are summarized in Table 1. In all cases, the wipe candidates were used as received from the manufacturer with no special cleaning of the wipe prior to evaluation.

2.2   Description of Surface Substrates

Three surrogate surfaces were utilized during the method optimization and validation stages of this effort. The primary surface was a commercially available gloss white glazed tile, measuring 108×108 mm. This tile was identified as part number SL10-44HCBP and was obtained from the American Olean Tile Company (Dallas, TX). The second surface was the previously described ceramic tile, spray painted with two coats of a flat black paint (Rust-Oleum, Vernon Hills, IL). These painted tiles had been prepared for another project, and the paint had aged for ~6 months before experiments were conducted. The third surface consisted of sections of a ton container that had been cut into sections measuring ~ 50×50 mm square and ~10 mm thick. Spiking was performed on the inner surface of the ton container section.

Table 1. Description of Materials Evaluated as Wipe Candidates

Wipe Candidate Identification	Description	Manufacturer Information
WC-1[a]	Type GF-6, 90 mm borosilicate glass fiber filter with inorganic binders	Whatman, Piscataway, NJ[b]
WC-2	Type GF/F, 47 mm borosilicate glass fiber filter without binders	Whatman, Piscataway, NJ[b]
WC-3	Type GF/D, 47 mm borosilicate glass fiber filter without binders	Whatman, Piscataway, NJ[b]
WC-4	Type A/E, 47 mm borosilicate glass fiber filter without binders	Pall Life Sciences, Port Washington, NY
WC-5	Grade 1, 90 mm filter paper	Whatman, Piscataway, NJ[b]
WC-6	Grade 113, 90 mm filter paper	Whatman, Piscataway, NJ[b]
WC-7	Grade 42, 55 mm filter paper	Whatman, Piscataway, NJ[b]
WC-8	Cellulose nitrate membrane filter, 47 mm	Whatman, Piscataway, NJ[b]
WC-9	Polycarbonate membrane filter, 47 mm	Whatman, Piscataway, NJ[b]
WC-10	PALLFLEX EMFAB membrane filter, 47 mm	Pall Life Sciences, Port Washington, NY
WC-11	NYLASORB nylon membrane filter, 47 mm	Pall Life Sciences, Port Washington, NY
WC-12	Cotton gauze pad, 2×2 in.	Johnson and Johnson, New Brunswick, NJ

a. This wipe was used during the original EDS sampling.
b. Whatman is now part of GE Healthcare Life Sciences.

2.3 Reagents

All study chemicals were used as received from the manufacturer. Sodium hydroxide (NaOH, CAS No. 1310-73-2, 99.99%, semiconductor grade) was obtained from Sigma-Aldrich (Milwaukee, WI). The proprietary CE buffer was purchased from Agilent Technologies (Santa Clara, CA).

The deionized water, ASTM Type I, was obtained from an in-house system (18 MΩ·cm, Nanopure, Barnstead, Dubuque, IA).

2.4 Preparation of Extraction Solution

The extraction solution was prepared by weighing 100 ± 5 mg of solid NaOH, and quantitatively transferring the NaOH to a 1 L class A volumetric flask containing ~500 mL of deionized water. A Teflon stir bar (12×3 mm) was added, and the mixture was stirred until all the solid NaOH dissolved. Once the solid NaOH dissolved and the solution had cooled back to room temperature, the volume was brought to the mark with deionized water. The extraction solution was sterilized using vacuum filtration through a 0.2 μm nylon filter and stored at ambient (~24 °C) temperature in a high density polypropylene plastic bottle.

2.5 Standards

Sodium cyanide (NaCN, ≥97.0%, CAS no. 143-33-9) and potassium cyanate (KOCN, ≥97.0%, CAS no. 590-28-3) were obtained from Sigma-Aldrich and were used as received from the manufacturer. When not in use, the neat materials were stored in a desiccator at ambient temperature (~24 °C). In this report, the free cyanide anion is abbreviated as CN and the free cyanate anion is abbreviated as OCN.

Primary stock solutions were prepared gravimetrically using Class A volumetric glassware. The primary stock solutions were prepared in deionized water, at concentrations of ~0.3 g/mL for CN and OCN, and the exact concentrations were recorded. The primary stock solutions were stored in amber glass vials at ~4 °C when not being used. Separate primary stock solutions were prepared for generation of the calibration curve, calibration verification standards, and spiking solutions. Working solutions were prepared volumetrically from the primary stock solution, using Class A pipets and volumetric flasks. Deionized water was used to dilute the primary stock solutions.

2.6 Determination of Target Analytes

An Agilent Technologies model 3D CE system, with an ultraviolet (deuterium lamp) diode array detector, was used to determine the quantities of CN and OCN during this study. The separation capillary was a piece of polyimide-coated fused silica with the polyimide coating removed at the optical window. The capillary dimensions were 64.5 cm (L_{tot}) $\times$ 50 μm i.d. Capillary zone electrophoresis (CZE) with indirect ultraviolet detection was used to determine the analytes. A proprietary CE buffer (Agilent Technologies) was used for all CE analyses in this study.

The CZE method selected for use in this project has been used extensively in other projects and found to be rugged and reliable.[6,7] The analytes are determined directly, without derivatization or extraction from the liquid phase. Samples were pressure-filtered through a 0.2 μm nylon Acrodisc filter (Pall Life Sciences), then the filtrate was diluted with mobile phase prior to analysis. The suitability of these filters was verified by analyzing the same mixed solution of CN and OCN, with and without the filtration step. There was no significant loss of either analyte when the solution was filtered.

2.7   Estimation of Precision and Accuracy

Precision and accuracy of analytical measurements are defined in several different ways by various regulatory agencies. In general, *accuracy* is defined as the degree to which a measured value approaches its true value and is most often expressed as percent recovery.[10] *Precision* is commonly defined as the standard deviation of multiple measurements at a given concentration level.[11] The approach used in this study adheres to Environmental Protection Agency (EPA) guidance on determining precision and accuracy in waste streams.[12] This approach requires that multiple replicates of spiked sample matrix be prepared and analyzed at a spike level that is at or below the reporting limit. A minimum of seven spike replicates and one unspiked matrix blank must be prepared. Recovery in the range of 70 to 130% is acceptable according to the EPA guidelines, but recoveries that are outside this range can be acceptable in instances where the analyte is unstable or the sample matrix is reactive.

2.8   Estimation of Detection Limits

In the analytical community, estimation of detection limits (DLs) is a an issue for lively discussion.[13,14] The approaches to estimating a DL range from the very simple, such as the concentration that gives a signal with a signal-to-noise ratio of three,[15] to more complicated approaches, such as using a weighted least-squares calibration design approach.[16] However, a complete discussion of the theory behind DLs is beyond the scope of this report. Interested readers are referred to a seminal paper on the subject of DLs.[17]

One approach for estimating a DL is that used by the EPA.[18,19] Multiple replicates (a minimum of seven) are prepared and processed using the *established* method. The *sample* standard deviation (SSD) is calculated then multiplied by the appropriate one-tailed Student's *t* statistic at the 99% confidence interval (CI); the resulting value is the method detection limit (MDL). The EPA defines the MDL as the "minimum concentration of substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero, and is determined from analysis of a sample in a given matrix containing the analyte". This EPA approach does not take into account the effects of high or low bias and does not control for the possibility of false negatives. The EPA is currently re-evaluating the use of this MDL approach.[20]

To estimate a DL in this study, a simple calibration design protocol was used that takes into account the effects of high and low bias and controls for both false positives and false negatives.[11] In this calibration design, at least seven replicates were prepared and analyzed at a minimum of three spike levels. The SSD of found analyte was then estimated for each spike

level and plotted against actual sample concentration. A linear regression model was fit to the data, and the sample standard deviation at zero concentration (SSD_0) was estimated by extrapolation. The DL at the 95% CI was then estimated as $3 \times SSD_0$.

3.   RESULTS AND DISCUSSION

        This section describes the experiments conducted during the optimization and validation of a method for the determination of free CN and OCN on surfaces using a wipe methodology. This method was successfully validated for the determination of trace levels of CN and OCN and is believed to be suitable for other chemicals generated during EDS demilitarization operations. The validated collection and extraction protocols are detailed in Section 3.4 of this report.

3.1   Initial Screening of Wipe Candidates

        The 12 wipe candidates, described in Table 1 of this report, were first evaluated by folding each wipe in half to determine if the material was too brittle for this application. In this initial screening, candidates WC-9 and WC-10 were eliminated from further consideration because they shattered when the membrane was folded in half. The second evaluation consisted of gently rubbing the wipe candidate on a section of ton container to determine if the wipe candidate would hold up to this action on a rough surface. Wipe candidates WC-5, WC-6 and WC-7 broke apart during this evaluation and were eliminated from further consideration. Four glass fiber filters were presented as candidates. Therefore, to reduce the number of glass fiber filters being evaluated, wipe candidates WC-2 and WC-3 were also eliminated. Wipe candidates WC-1 and WC-4 were the glass fiber filters selected for further evaluation in this study. This selection allowed a comparison of glass fiber filter material with and without a binding agent. Out of the initial 12 wipe candidates, 5 wipes were downselected for further evaluation.

        An experiment used to examine the sorption of CN and OCN from caustic solution (the 0.01 % NaOH extraction solvent) was conducted to screen whether CN and OCN could be efficiently extracted from the wipe candidates. In this experiment, a single batch of caustic solution was prepared and spiked to a nominal level of 150 mg/L each of CN and OCN. Duplicate vials were prepared by placing 20 mL of this spiked caustic solution into 40 mL vials then adding the wipe candidates. In addition to the wipe samples, duplicate vials of the caustic solution without any wipe material were prepared as positive controls. Samples were periodically removed from each vial, filtered, and analyzed using the method described in Section 2.6 of this report. In addition to the samples and controls, two caustic reagent blanks were also prepared and analyzed.

        In all cases, no CN or OCN was detected in any of the caustic reagent blank samples ($n = 2$). The average ($n = 26$) recovery for the continuing calibration verification (CCV) samples was 95.5% and ranged from 72.0 to 112%. No trending over time was observed in the control samples, and the average ($n = 16$, ±SSD) concentrations were determined to be 145 ± 3.4 and 136 ± 5.2 mg/L for CN and OCN, respectively. Using the regression function in Microsoft Excel, the Student's t statistics were −0.3229 and −0.1007 for the slopes of the control linear

regression lines for CN and OCN, respectively. The critical value ($t_{0.05/2,14}$) of the Student's t statistic was 2.14, so the critical value was not exceeded.[21] This demonstrated that the slopes of both linear regression lines were not significantly different from zero at the 95% CI. The wipe candidate sorption profiles are illustrated in Figure 1. There was a significant loss of CN and OCN from the spiked solution when it was exposed to wipe candidates WC-1 and WC-4, the two glass fiber filter candidates. Using a first-order kinetics model,[22] the solution half-lives of CN and OCN were estimated to be ~1.2 h when exposed to WC-1 and ~3.9 h when exposed to WC-4. The two polymeric wipe candidates, WC-8 and WC-11, showed an initial loss of CN and OCN at the first sampling point relative to the control values, but there was no additional loss over time. The recoveries ranged from 82.3 to 86.0% relative to the average control values. Wipe candidate WC-12 showed the highest recovery with an average ($n = 32$, ±SSD) recovery of $97.1 \pm 2.80\%$. No significant trends were observed over the course of the experiment with WC-12. Using the regression function in Excel, the Student's t statistics were –0.7254 and –0.9521 for the slopes of the WC-12 linear regression lines for CN and OCN, respectively. The critical value ($t_{0.05/2,14}$) of the Student's t statistic was 2.14, so the critical value was not exceeded.[21] This demonstrated that the slopes of both linear regression lines were not significantly different from zero at the 95% CI. The lack of sorption with wipe candidate WC-12, coupled with its flexibility and durability, resulted in it being downselected for use in this method.
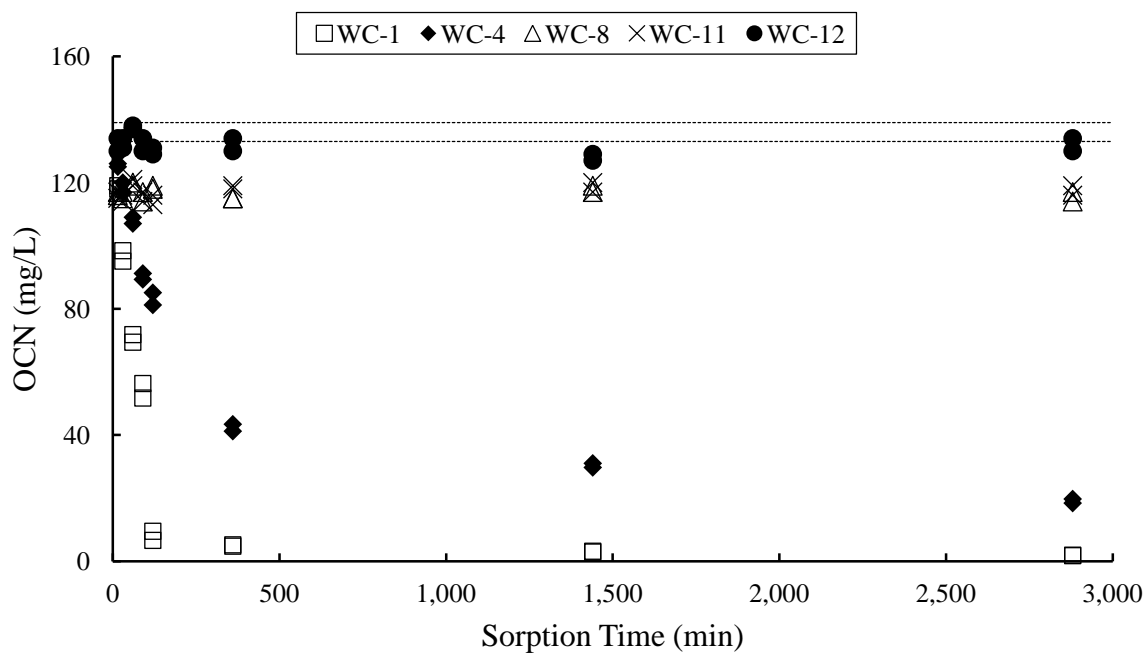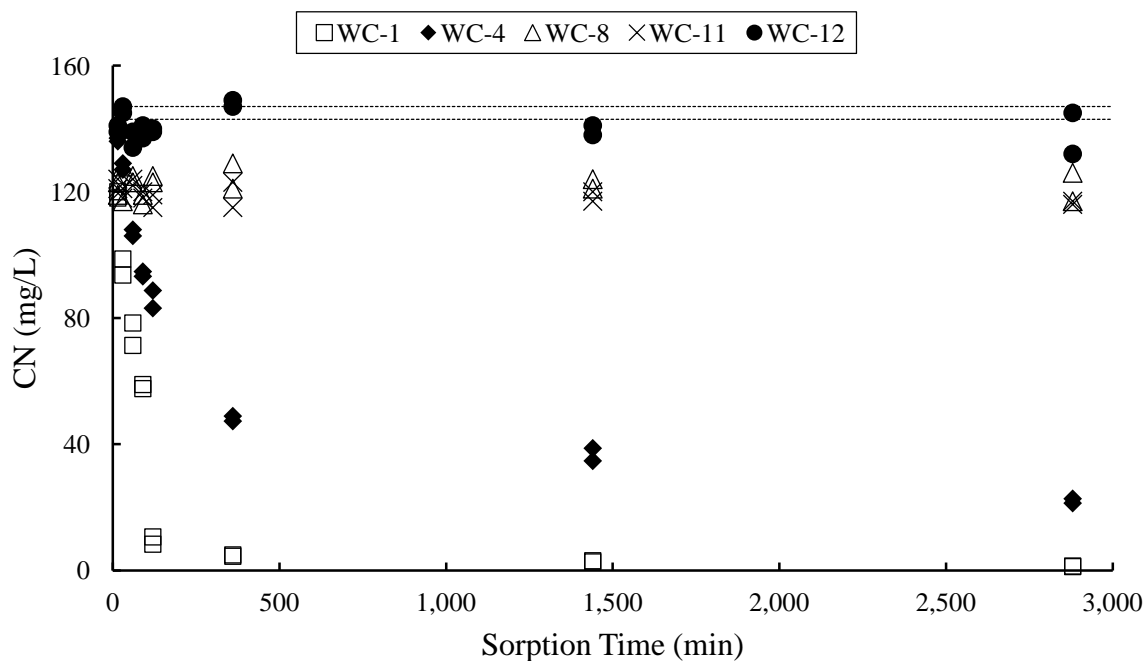
Figure 1. Sorption of target analytes from caustic extraction solution. Upper panel shows CN and lower panel shows OCN. The horizontal dashed lines represent the 95% CI of the control (no wipe) concentration.

3.2   Optimization of Extraction Parameters

In a preliminary experiment, extraction efficiency data were generated by first dampening wipe candidate WC-12 with 0.5 mL of deionized water then spiking a mixed working solution of CN and OCN onto the wipe and letting the spike age for 15 min before extracting the sample. The extraction was accomplished by adding a Teflon stir bar (12×3 mm) to the vial and stirring for various times at ambient (~24 °C) temperature. The extraction times were 15, 30, 45, and 60 min, and each treatment was performed in duplicate. The spiking solution was prepared in deionized water, and the nominal spike amount was 1.5 mg for both CN and OCN.   In addition to the spiked wipes, one unspiked wipe was stirred for 60 min to act as a worst-case wipe matrix blank. Two laboratory control spikes (LCSs) were prepared, which consisted of 10 µL spiking solution added directly to 10 mL of extraction solution. The average ($n = 2$) LCSs were 1.42 and 1.33 mg, respectively, for CN and OCN. No CN or OCN was detected in the wipe matrix blank. The average ($n = 8$) recovery of calibration check standards was 98.5% and ranged from 92.0 to 103%. In all cases ($n = 16$), the spike recovery was low and variable, ranging from 5 to 13%. It was concluded that stirring was not an adequate method to extract these wipes, and a more energetic approach, such as sonication, was required.

Spike recovery data, as a function of sonication time, were generated by first dampening wipe candidate WC-12 with 0.5 mL of deionized water then spiking a mixed working solution of CN and OCN onto wipe candidate WC-12 and letting the spike age for 15 min before sonicating the sample. The sonication times ranged from 1 to 120 min, and each treatment was performed in duplicate. The spiking solution was prepared in deionized water, and the nominal spike amount was 1.5 mg for both CN and OCN. In addition to the spiked wipes, three unspiked wipes were sonicated for 120 min to act as worst-case wipe matrix blanks. Four LCSs were prepared, which consisted of 10 µL spiking solution added directly to 10 mL of extraction solution. The LCS samples were used to establish the theoretical spike level.

In all cases, no CN or OCN was detected in any of the wipe matrix blank samples ($n = 3$). The average ($n = 26$) recovery for the CCV samples was 96.8% and ranged from 77.0 to 116%. The recovery data are illustrated in Figure 2, which shows that sonication time has a significant effect on spike recovery of both CN and OCN. Although spike recovery continued to slowly increase after 60 min, a sonication time of 60 min was selected for this method. Doubling the sonication time to 120 min only resulted in a recovery increase of ~12%.

Spike recovery data, as a function of spike aging time, were generated by spiking a mixed working solution of CN and OCN onto wipes then letting the spike age for various times before extracting the wipes using the procedure outlined in Section 3.3 of this report. The spike aging times ranged from 15 to 2880 min. An additional variable was also evaluated during this experiment. The wipes were spiked either dry or after they had been dampened by pipetting 0.5 mL of deionized water onto the wipe. The spiked wipe samples were stored in individual sealed vials at ambient (~24 °C) temperature. The spiking solution was prepared in deionized water, and the nominal spike amount was 1.5 mg for both CN and OCN. In addition to the spiked wipes, three unspiked wipes were processed to act as wipe matrix blanks. Four LCSs were prepared, which consisted of 10 µL of spiking solution added directly to 10 mL of extraction solution. The LCS samples were used to establish the theoretical spike level.

In all cases, no CN or OCN was detected in any of the wipe matrix blanks ($n = 3$). The average ($n = 22$) recovery for the CCV samples was 86.5% and ranged from 81.0 to 115%. The recovery data are illustrated in Figure 3 and demonstrate significant loss in recovery as the spike aged on the dry wipe. There was no significant loss in recovery if the wipe was dampened prior to being spiked. The phenomenon of decreasing recovery with increasing sample age was well documented in the literature for pesticides and other organic chemicals.[23,24] It has also been recently documented that this aging phenomenon can occur when the chemical warfare agent VX is allowed to interact with clay minerals.[25] These data demonstrate that the wipes should be dampened to prevent CN and OCN from sorbing to the wipe.

To help distinguish whether the loss of CN recovery on the dry wipe was due to degradative loss or a sorptive/complexation process, the experiment was repeated using CN only. The wipes were then analyzed by an EPA method for total CN.[26] In this experiment, spiking was conducted such that all samples were digested and analyzed on the same day. The samples were sent out to a laboratory certified to conduct these types of analyses, and the results are illustrated in Figure 4. The recovery of total CN over the course of the experiment was unchanged and had an overall average ($n = 16$, ±SSD) recovery of $97.2 \pm 3.19\%$. Using the regression function in Excel, the Student's t statistic was -1.5680 for the slope of the linear regression line for total cyanide. The critical value ($t_{0.05/2,14}$) of the Student's t statistic was 2.14, so the critical value was not exceeded.[21] This demonstrated that the slope of the linear regression line was not significantly different from zero at the 95% CI. These data demonstrated that the CN was not degrading, but was becoming unextractable over time. It is not known whether this was due to interaction with the wipe material itself or to the presence of metal contaminants in the wipe material.
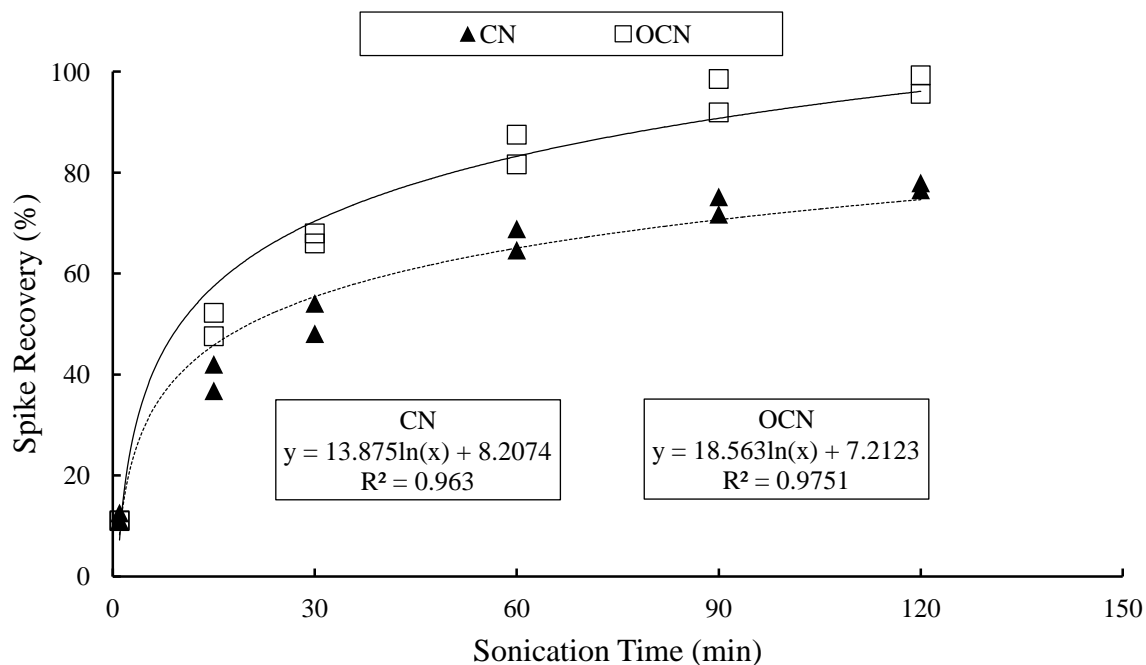
Figure 2. Spike recovery as a function of sonication time. The wipe candidate was WC-12, wipes were dampened prior to being spiked, and the spike was aged for 15 min before it was extracted.
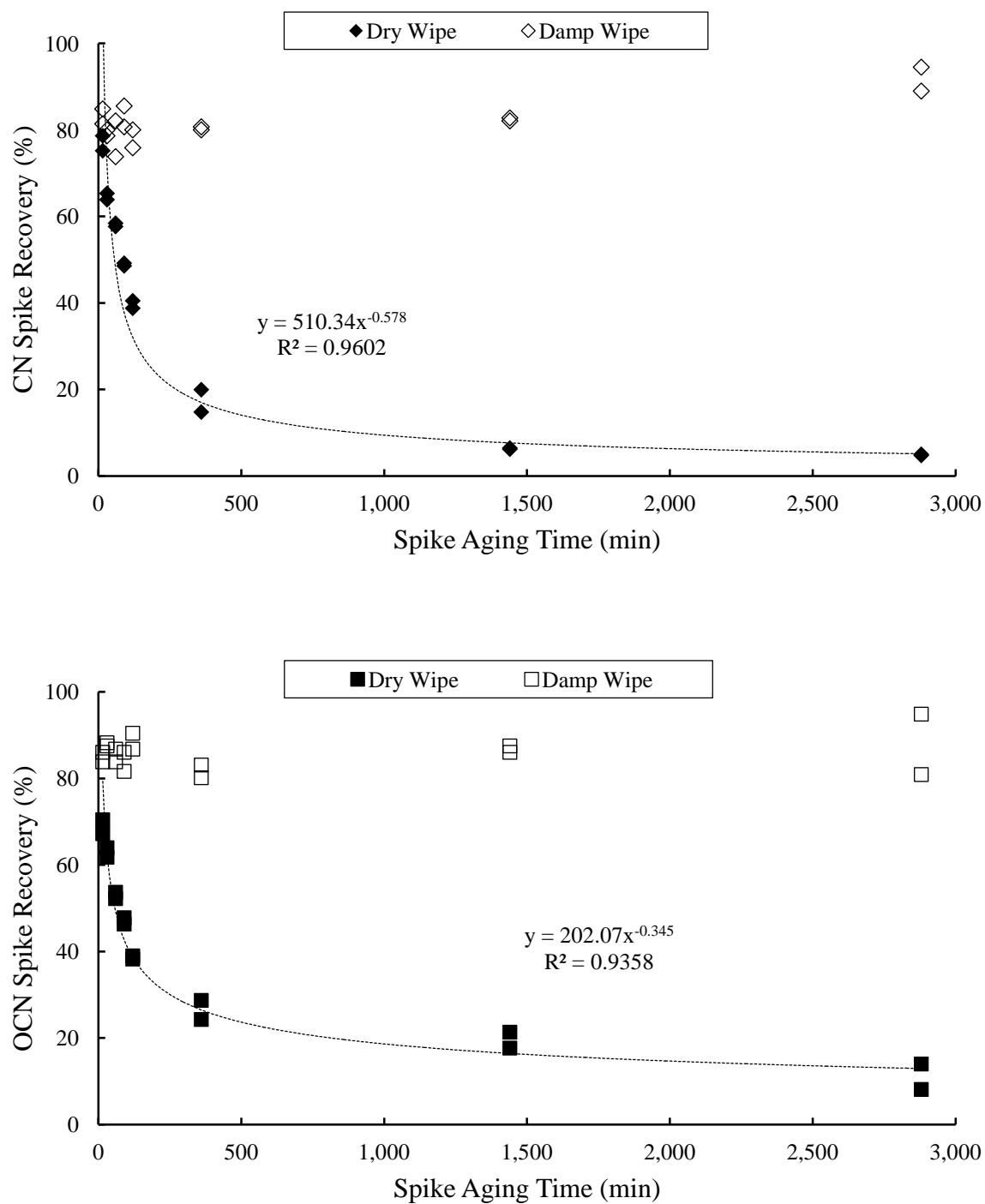
Figure 3. Spike recovery as a function of spike aging time. Upper panel shows CN and lower panel shows OCN. The wipe candidate was WC-12, and the wipes were sonicated for 60 min.
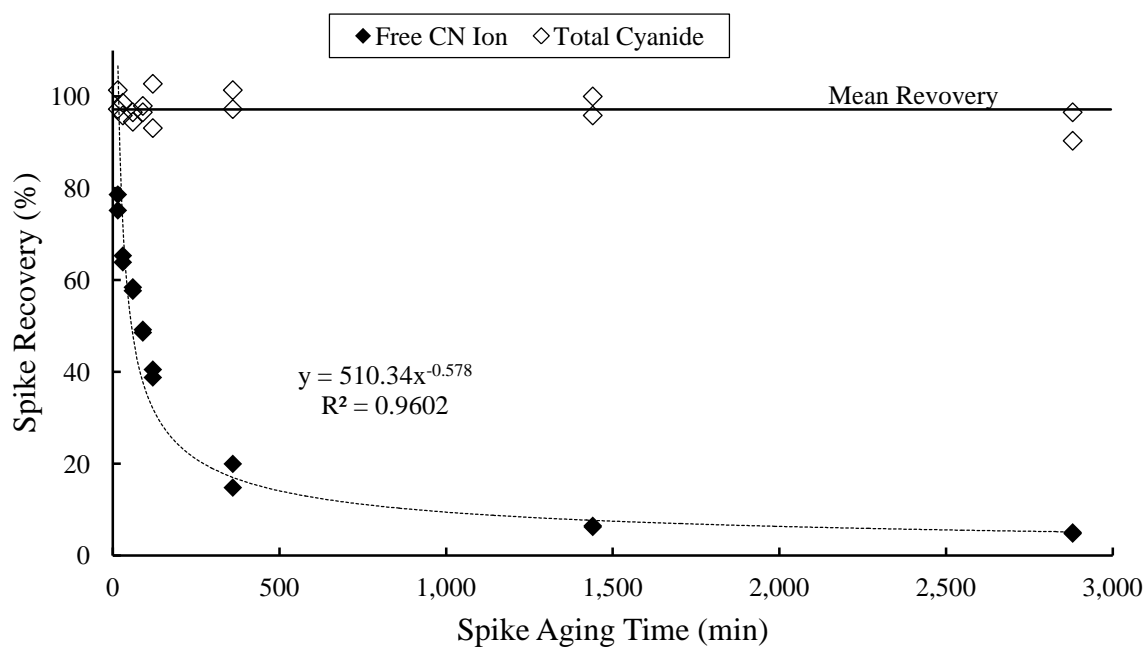
Figure 4. Spike recovery from dry wipe. Comparison of CE method for free CN ion and EPA method for total cyanide.

3.3   Validation of Method

        This section describes the experiments conducted during the validation of a wipe method for the determination of residual free CN and OCN on surfaces. The validation stage was done with a single wipe candidate, WC-12. The precision and accuracy data indicated that the entire analytical process (collection, extraction, and analysis) was under control and suitable for quantitative analysis of residual free CN and OCN from surfaces.

3.3.1   Calibration Model

        The external calibration models were established by preparation and analysis of a set of standards on three different days over the course of two weeks. On every day of preparation, each standard concentration was analyzed two times. A total of six concentrations (4.24, 8.48, 21.2, 42.4, 84.8, and 212 mg/L) of CN and five concentrations (4.14, 8.28, 20.7, 41.4, and 82.8 mg/L) of OCN were analyzed during this modeling effort. The instrument detection limits (IDLs) were estimated to be 4.2 and 4.1 mg/L for CN and OCN, respectively. Example calibration curves and electropherograms are illustrated in Figure 5.

        The storage stability of CN and OCN primary stock solutions was evaluated by preparing both individual primary stock solutions of CN and OCN and a mixed primary stock solution containing both CN and OCN. In all cases, the concentration of each primary stock was ~0.3 g/mL. Each stock solution was split between two amber glass vials, with one stored at ambient (~24 °C) temperature and the other one stored at ~4 °C. At various times, aliquots were removed from each vial, diluted, and analyzed using the procedure described in Section 2.6 of this report. The storage times ranged from 0 to 28 days, and the Day 0 time point was ~30 min after the primary stocks were prepared. The Day 0 samples were used to establish the initial concentrations of CN and OCN. In addition to the primary stock solutions, two deionized water reagent blanks were prepared and analyzed with each set of samples.

        In all cases, no CN or OCN was detected in any of the reagent blanks ($n = 14$). The average ($n = 18$) recovery for the CCV samples was 91.4% and ranged from 82.0 to 97.1%. The stability data are illustrated in Figures 6 and 7 and demonstrate that the primary stock solutions were stable for at least 30 days when stored at either ambient (~24 °C) temperature or ~4 °C when the solutions were protected from light. Using the regression function in Excel, the Student's t statistics ranged from –0.2000 to 1.9476 for the slopes of the linear regression lines. The critical value ($t_{0.05/2,5}$) of the Student's t statistic was 2.57, so the critical value was not exceeded.[21]   This demonstrated that the slopes of all linear regression lines were not significantly different from zero at the 95% CI. The overall average ($n = 52$, ±SSD) recovery of the stock solutions was 94.5 ± 4.37%.
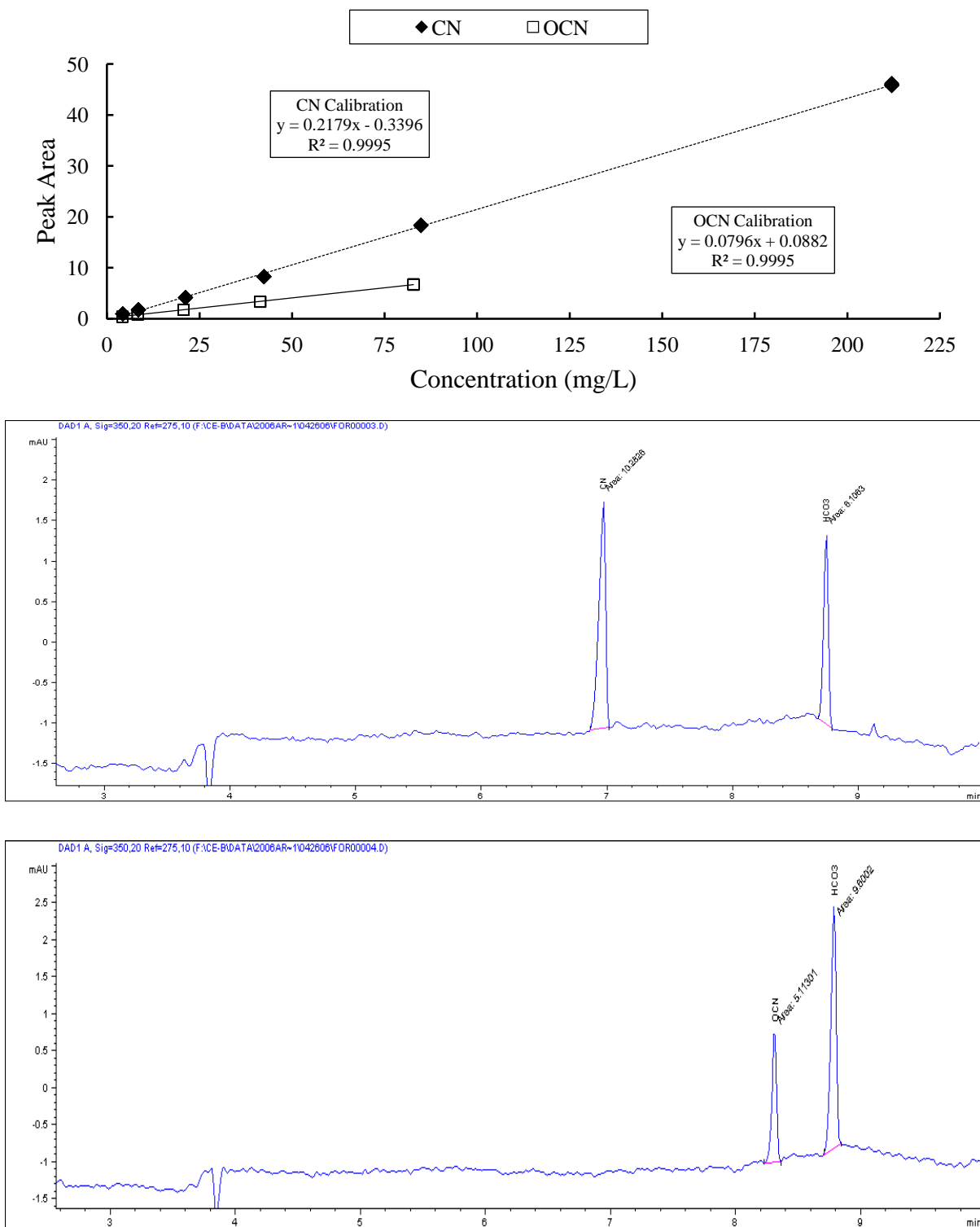
Figure 5. Example external calibration curves and electropherograms. Upper panel shows the calibration curves, middle panel shows the 42.4 mg/L CN standard electropherogram, and lower panel shows the 41.4 mg/L OCN standard electropherogram.

Figure 6. Storage stability of individual primary stock solutions. Upper panel shows the results from storage at ambient (~24 °C) temperature and lower panel shows the results from storage at ~4 °C. The slopes were not significantly different from zero at the 95% confidence level.

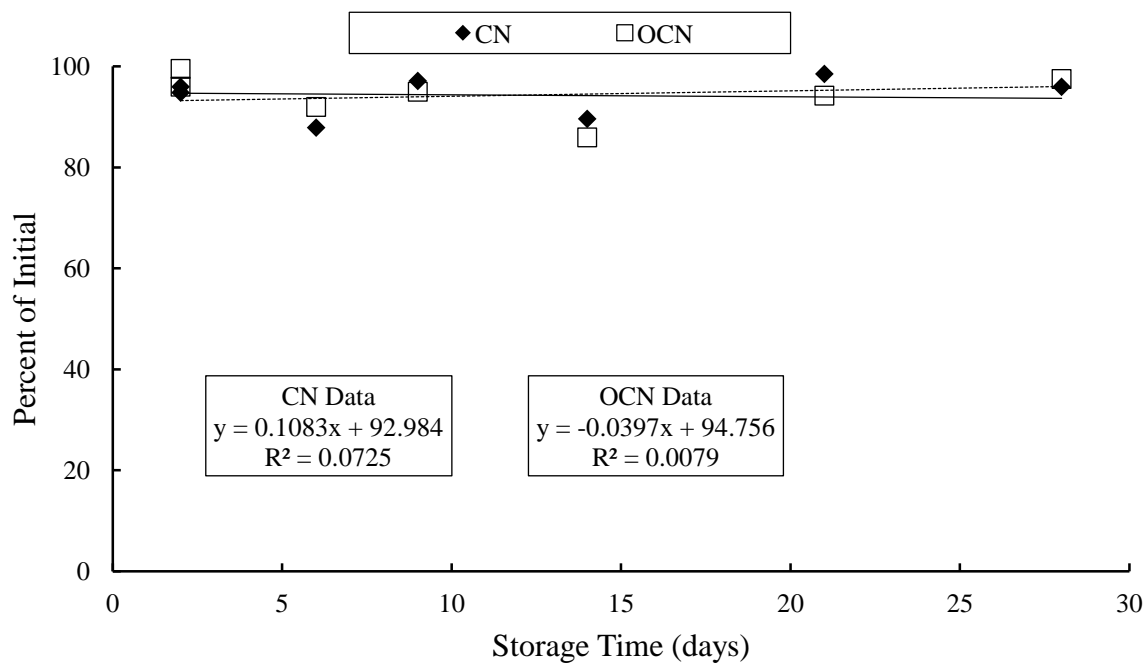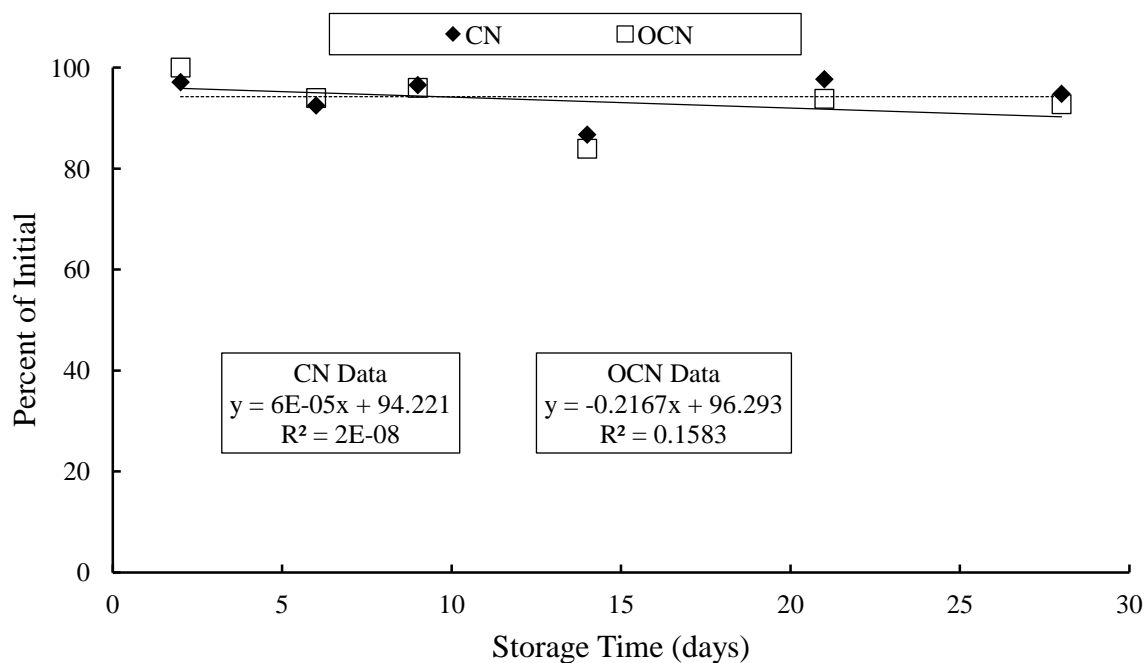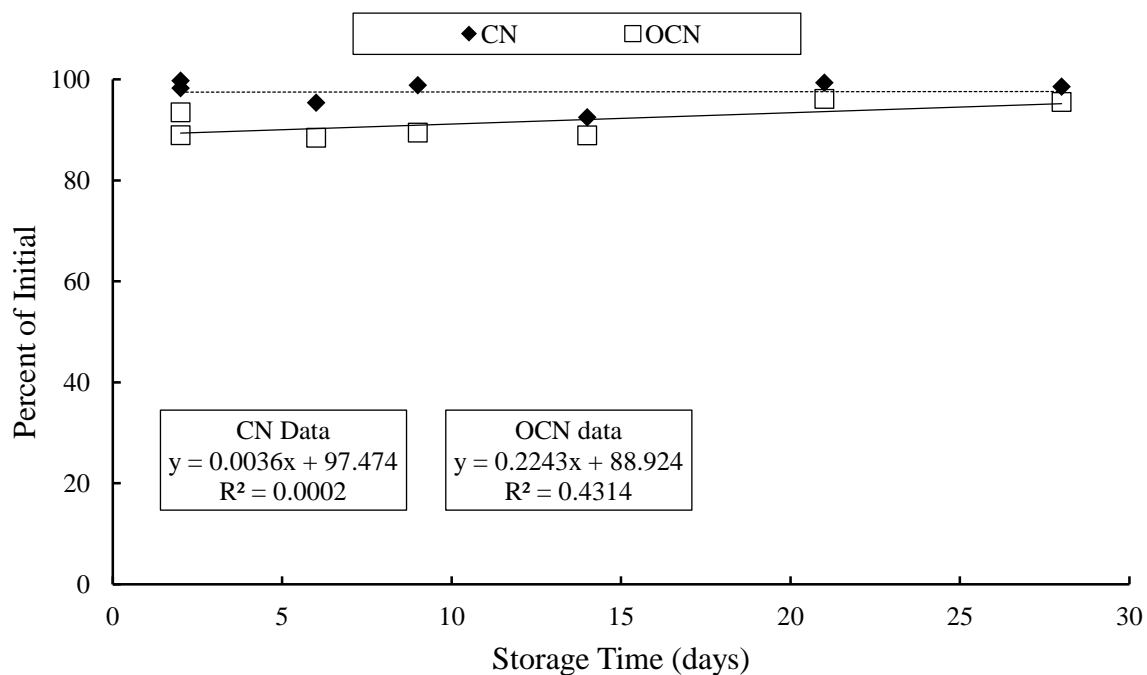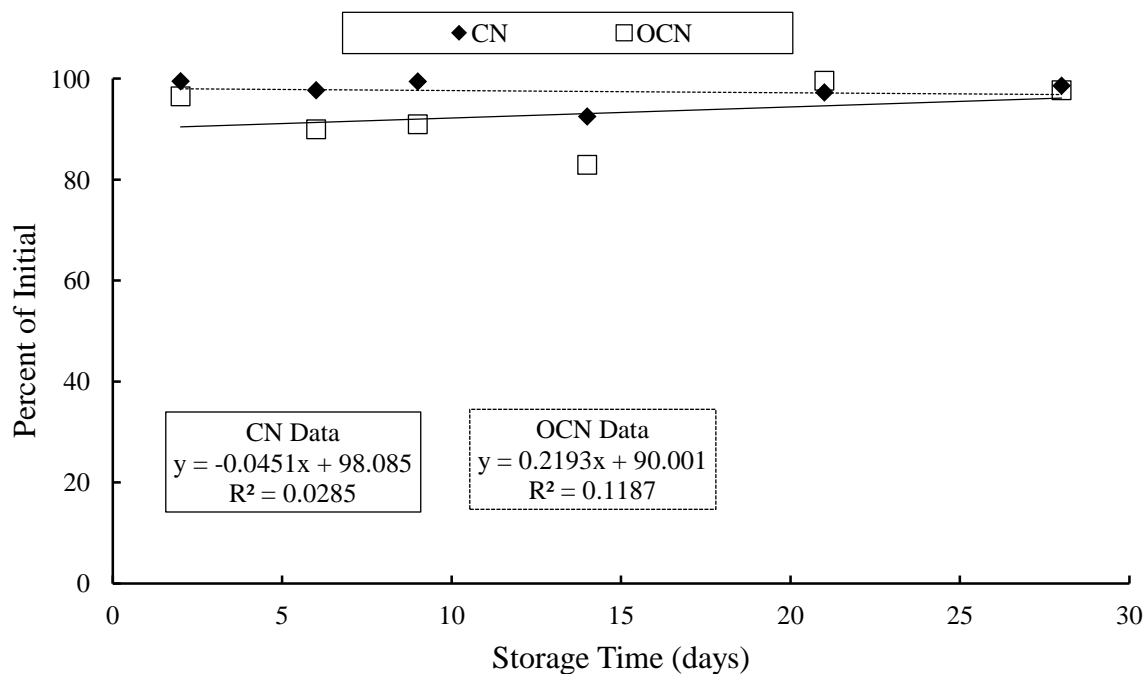Figure 7. Storage stability of a mixed primary stock solution. Upper panel shows the results from storage at ambient (~24 °C) temperature and lower panel shows the results from storage at ~4 °C. The slopes were not significantly different from zero at the 95% confidence level.

3.3.2   Precision and Accuracy of Spike Recovery

Precision and accuracy data were generated by spiking a mixed working solution of CN and OCN onto wipes, then letting the spike age for 15 min before extracting the compounds from the wipes using the procedure outlined in Section 3.4.2 of this report. Spiking solutions were prepared in deionized water at different concentrations, but the spike volume of 10 µL was maintained as constant for all spike levels. Multiple replicates ($n = 10$) were independently prepared, extracted, and analyzed at seven nominal spike levels ranging from 0.25 to 1.75 mg per wipe. In addition to the spiked wipes, three unspiked wipes were processed to act as matrix blanks. Three LCS samples were prepared for each spike level and consisted of adding 10 µL of spiking solution directly to 10 mL of extraction solution. The LCS samples were used to establish the theoretical spike level.

In all cases, no CN or OCN was detected in any of the blank samples ($n = 3$). The average ($n = 26$) recovery for the CCV samples was 96.6% and ranged from 79.0 to 117%. The precision and accuracy data are summarized in Table 2. The average recovery of CN across all spiking levels was 76.6%, with a 95% CI of 75.2 to 78.1%. The average recovery of OCN across all spiking levels was 76.7%, with a 95% CI of 75.4 to 78.0%. The overall spike recovery was 76.7%, with a 95% CI of 75.7 to 77.6%. There was no significant difference in spike recovery as a function of spike amount, as illustrated in Figure 8. Using the regression function in Excel, the Student's t statistics were 0.9499 and –3.330 for the slopes of the linear regression lines for CN and OCN, respectively. The critical value ($t_{0.05/2,68}$) of the Student's t statistic was between 1.98 and 2.02, so the critical value was not exceeded.[21] This demonstrated that the slopes of both linear regression lines were not significantly different from zero at the 95% CI. Evaluation of the precision and accuracy data indicated that the extraction and analysis portions of the method were under control and were suitable for quantitative analysis of residual CN and OCN from this wipe material.

Using the precision data in Table 2 for the lowest four spike amounts and the average LCS values, the extraction detection limits (EDLs) were estimated using the approach outlined in Section 2.8 of this report. This estimation is illustrated in Figure 9. The EDLs were estimated to be 0.05 and 0.04 mg per wipe for CN and OCN, respectively. These EDLs were consistent with the CE IDL as described in Section 3.3.1 of this report.

Table 2. Precision and Accuracy Data for Spike Recovery from Wipes. Precision is the SSD of the determined concentration. Accuracy is the average ($n = 10$) percent recovery relative to the average LCS amount.

CN Spike Level[a] (mg)	Precision (mg)	Accuracy	
		(%)	95% CI[b]
0.235	0.0227	73.1	±6.9
0.470	0.0213	75.2	±3.2
0.678	0.0265	80.2	±2.8
1.04	0.0317	79.9	±2.2
1.17	0.0514	74.4	±3.1
1.51	0.0922	75.8	±4.4
1.71	0.107	77.7	±4.5

a. Determined by analysis of triplicate LCS.
b. The 95% CI calculated by Excel 2007.

OCN Spike Level[a] (mg)	Precision (mg)	Accuracy	
		(%)	95% CI[b]
0.208	0.0169	78.9	±5.8
0.430	0.0192	76.4	±3.2
0.630	0.0217	81.0	±2.5
0.918	0.0274	77.0	±2.1
1.07	0.0238	76.2	±1.6
1.35	0.0738	73.3	±3.9
1.53	0.0799	74.0	±3.7

a. Determined by analysis of triplicate LCS.
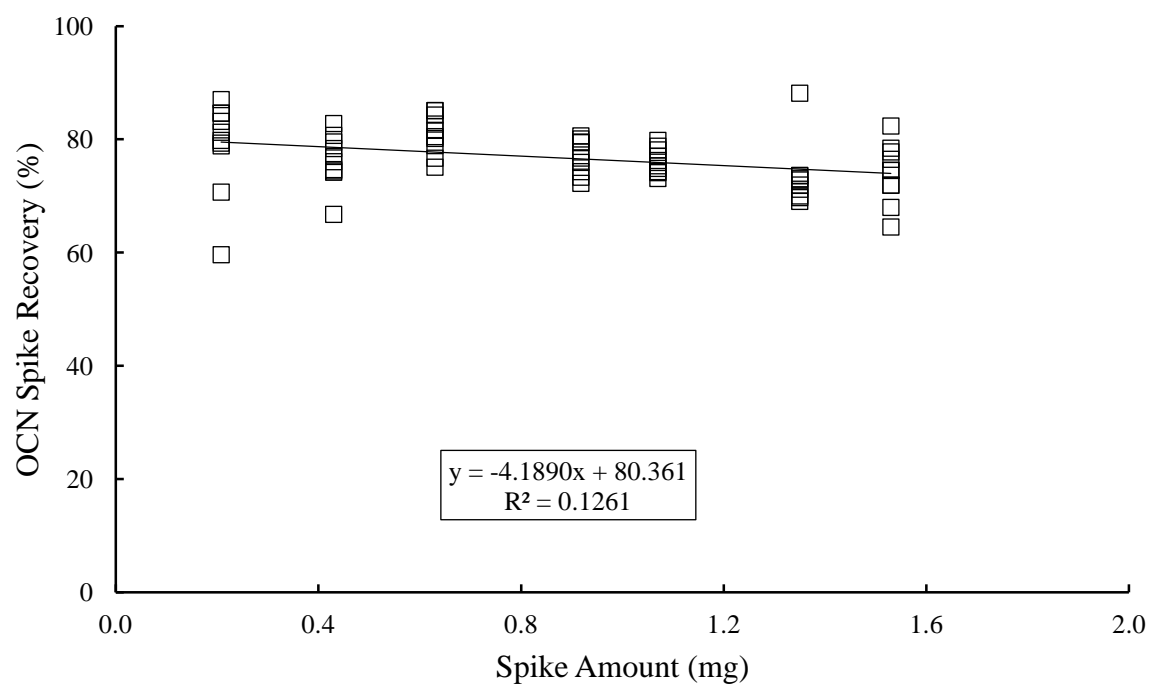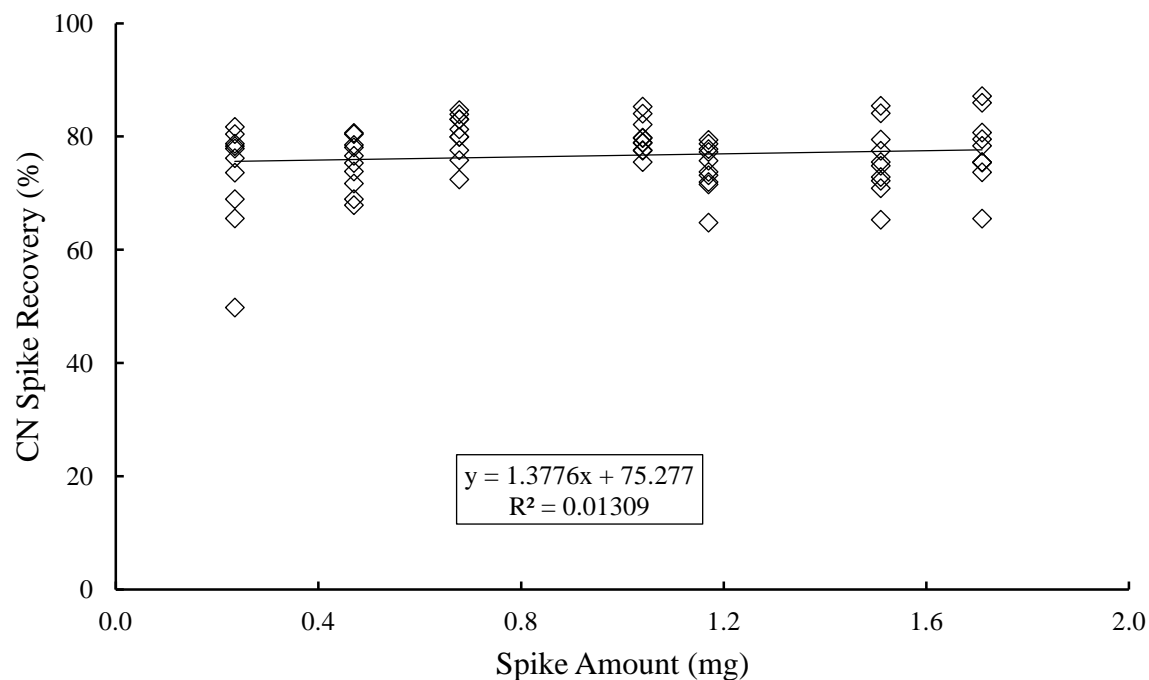b. The 95% CI calculated by Excel 2007.

Figure 8. Spike recovery as a function of spike amount. Upper panel shows CN and lower panel shows OCN. The slopes are not significantly different from zero at the 95% confidence level.
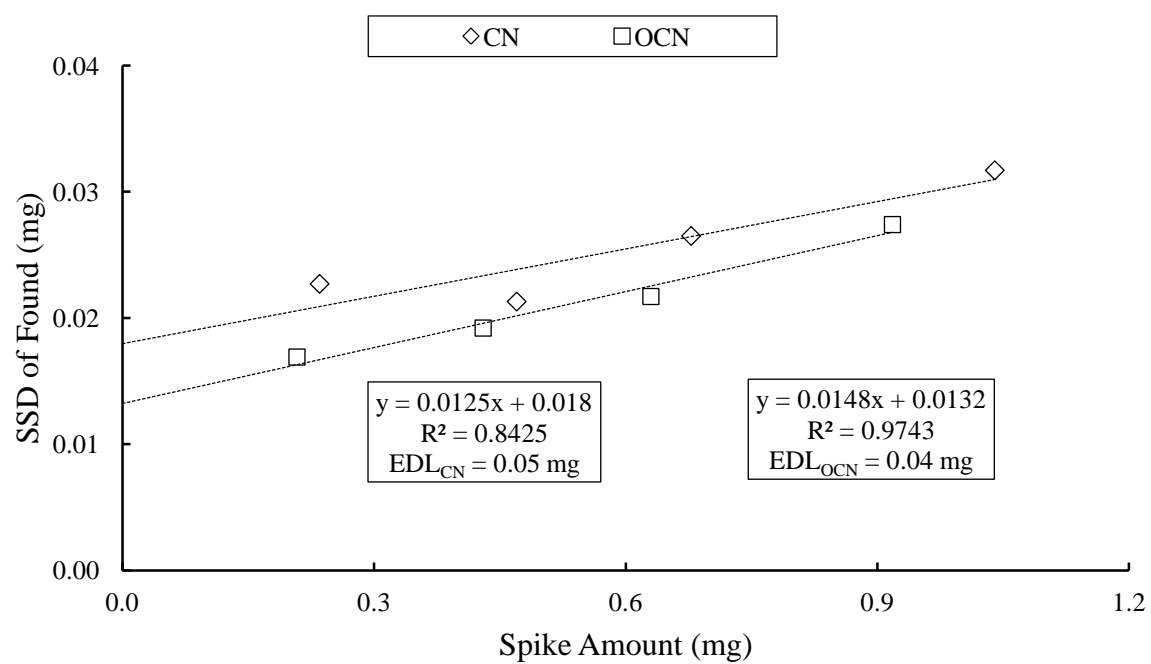
Figure 9. Estimation of EDL.

3.3.3   Storage Stability of Spiked Wipes

        Storage stability data were generated by spiking a mixed working solution of CN and OCN onto wipes, then letting the spike age for various times before extracting the wipes using the procedure outlined in Section 3.4.2 of this report. The aging times ranged from 0 to 32 days, with the Day 0 time point being 15 min after the wipe was spiked. The spiked wipe samples ($n = 4$ for each time point) were stored in individual sealed vials at ambient (~24 °C) temperature. In addition to the wipes stored at ambient temperature, a set of wipes were also stored for 32 days at –20 °C. The spiking solution was prepared in deionized water, and the nominal spike amount was 1.5 mg for both CN and OCN. In addition to the spiked wipes, three unspiked wipes were processed on Day 0 to act as blanks. Four LCS samples were prepared, which consisted of 5 µL of spiking solution added directly to 10 mL of extraction solution. The LCS samples were used to establish the theoretical spike level.

        In all cases, no CN or OCN was detected in any of the blank samples ($n = 3$). The average ($n = 50$) recovery for the CCV samples was 88.6% and ranged from 72.3 to 118%. The recovery data are illustrated in Figure 10 and demonstrate significant loss in recovery as the spike aged. On average, the loss in recovery during storage at ambient temperature was ~1.2% per day. This phenomenon of decreasing recovery with increasing sample age was well documented in the literature for pesticides and other organic chemicals.[25,26] It has also been recently documented that this aging phenomenon can occur when the chemical warfare agent VX is allowed to interact with clay minerals.[25] Storage of the spiked wipes at –20 °C enhanced the recoveries of both CN and OCN, resulting in an overall average recovery ~27% greater than when the wipes were stored at ambient temperature. These data demonstrated that once the wipes are collected, they should not be stored for extended times before being extracted. An alternative is to collect the wipe sample and immediately place it into a vial containing 10 mL of caustic solution. The sorption experiments described in Section 3.1 of this report, and the stock solution experiments described in Section 3.3.1 of this report suggest that neither CN nor OCN will bind to the wipe and the analytes will not degrade in the caustic solution.

        To help distinguish whether the loss of CN recovery during storage was due to degradative loss or a sorptive/complexation process, the experiment was repeated using CN only. The wipes were then analyzed in accordance with an EPA method for total CN.[26] In this experiment, the aging times were 0, 10, 20, and 30 days, and spiking was conducted such that all samples were digested and analyzed on the same day. The samples were sent to a laboratory certified to conduct these types of analyses, and the results are illustrated in Figure 11. The recovery of total CN over the 30 days of storage was unchanged, and had an overall average ($n = 12$, ±SSD) recovery of 95.2 ± 3.65%. These data demonstrated that the CN was not degrading, but was becoming unextractable over time. It is not known whether this was due to interaction with the wipe material itself or to presence of the metal contaminants in the wipe material.
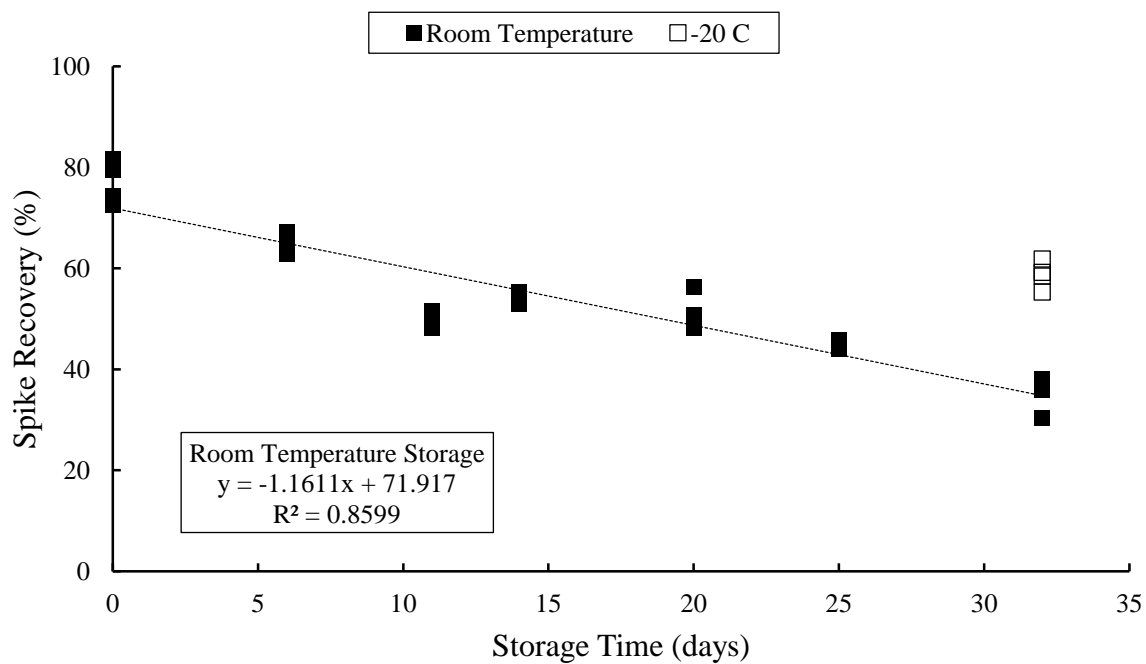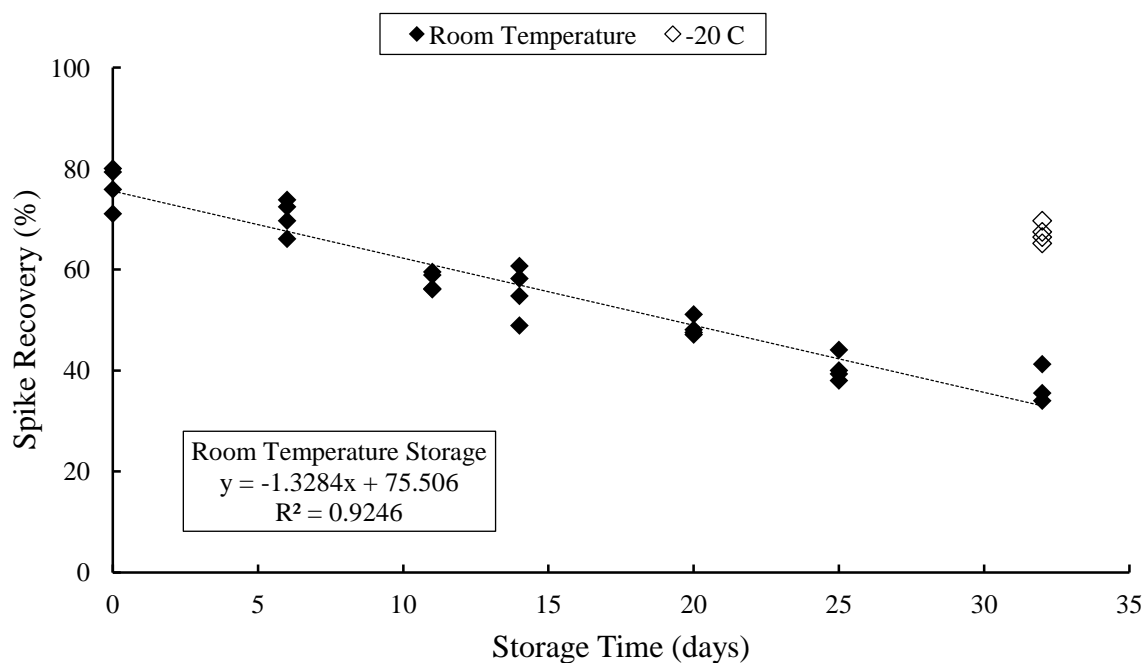
Figure 10. Storage stability of spiked wipe samples. Upper panel shows CN and lower panel shows OCN. Open symbols represent wipes stored at –20 °C.
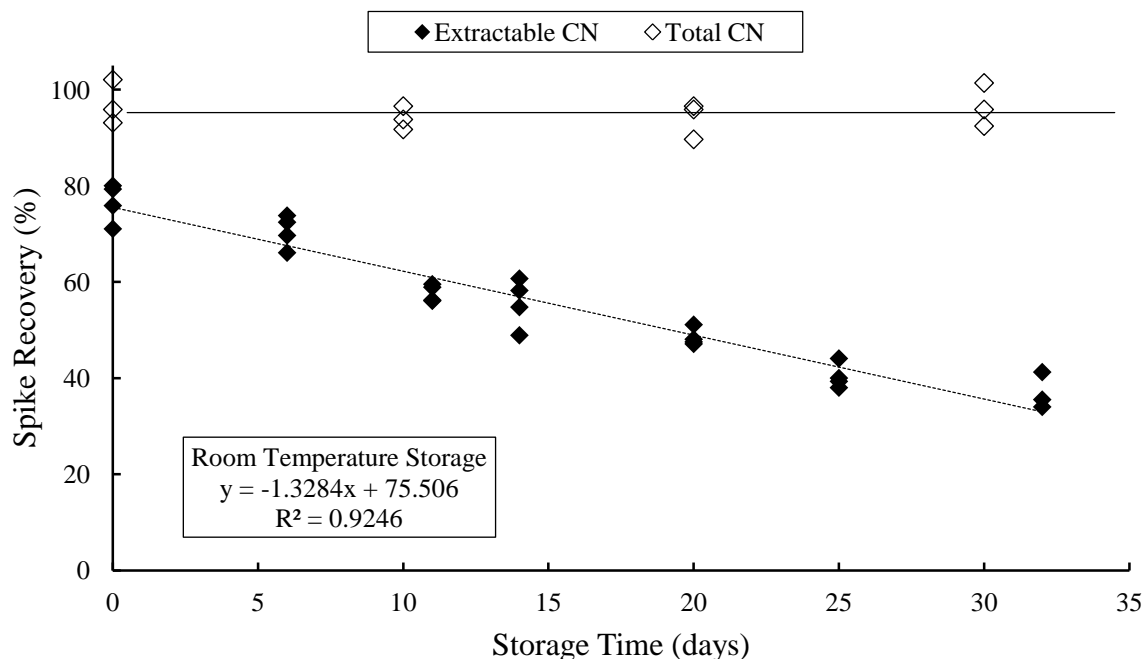
Figure 11. Recovery of free extractable cyanide and total cyanide over time. Horizontal line represents the average recovery for total CN.

3.3.4   Storage Stability of Spiked Coupons

Storage stability data were generated by spiking a mixed working solution of CN and OCN onto glazed ceramic tiles and ton container sections (called "coupons"). The spike solution was allowed to age for various times before the coupons were wiped using the procedure outlined in Section 3.4.1 of this report. The aging times ranged from 0 to 24 h, with the 0 h time point at 15 min after the coupon was spiked. The spiked coupons ($n = 2$ for each time point) were stored in individual sealed containers at ambient (~24 °C) temperature. The spiking solution was prepared in deionized water, and the nominal spike amount was 1.5 mg for both CN and OCN. In addition to the spiked coupons, one unspiked coupon of each type was processed after 24 h of storage to act as a matrix blank. Four LCS samples were prepared that consisted of 10 µL of spiking solution added directly to 10 mL of extraction solution. The LCS samples were used to establish the theoretical spike level.

In both cases, no CN or OCN was detected on either of the unspiked coupons. The average ($n = 34$) recovery for the CCV samples was 85.3% and ranged from 70.4 to 114%. The recovery data are illustrated in Figure 12 and demonstrated no significant loss in recovery from the glazed ceramic tile as the spike aged. The average ($n = 10$, ±SSD) recoveries were 46.0 ± 6.51 and 49.4 ± 4.01% for CN and OCN, respectively. The overall average ($n = 20$, ±SSD) recovery for both CN and OCN from glazed ceramic tile was 47.7 ± 5.54%. The recovery from the ton container coupon was significantly lower than that of the ceramic tile, with an average ($n = 4$, ±SSD) overall recovery at the 0 h time point of 25.1 ± 6.63%. The overall average ($n = 4$,

±SSD) recovery after 1 h of aging was $8.48 \pm 1.694\%$. There was no CN or OCN detected in the 2, 6, or 24 h time-point samples. The complexation of free CN and OCN with metals, especially iron and copper, was well documented in the literature.[27,28] The ton containers are made from common steel, so the most likely cause of the low recoveries from the ton container coupons was complexation with iron.
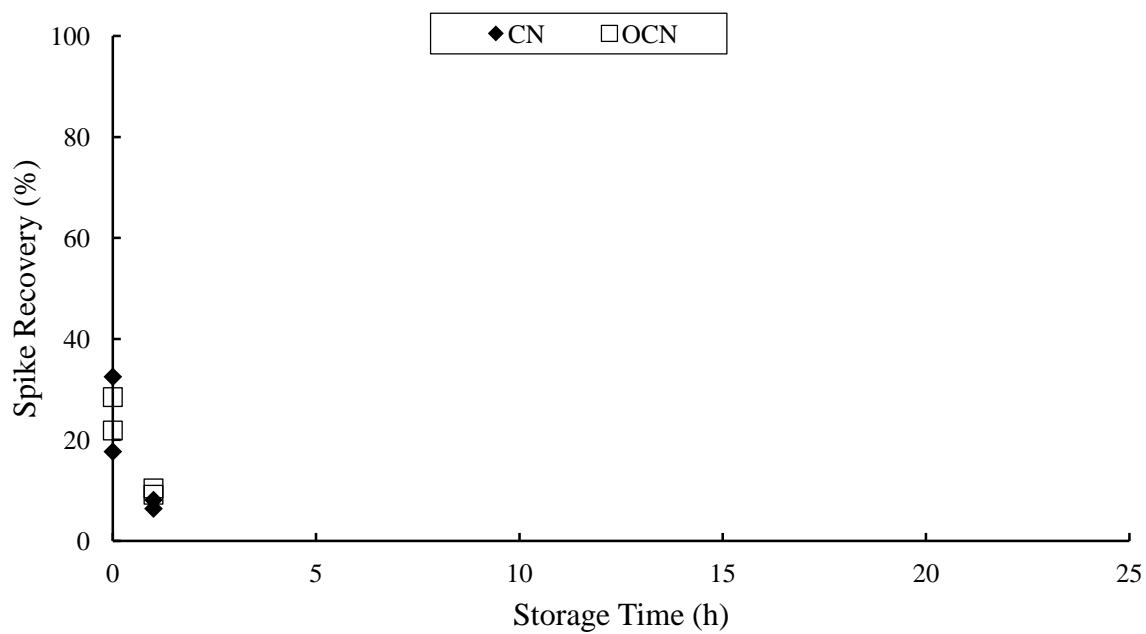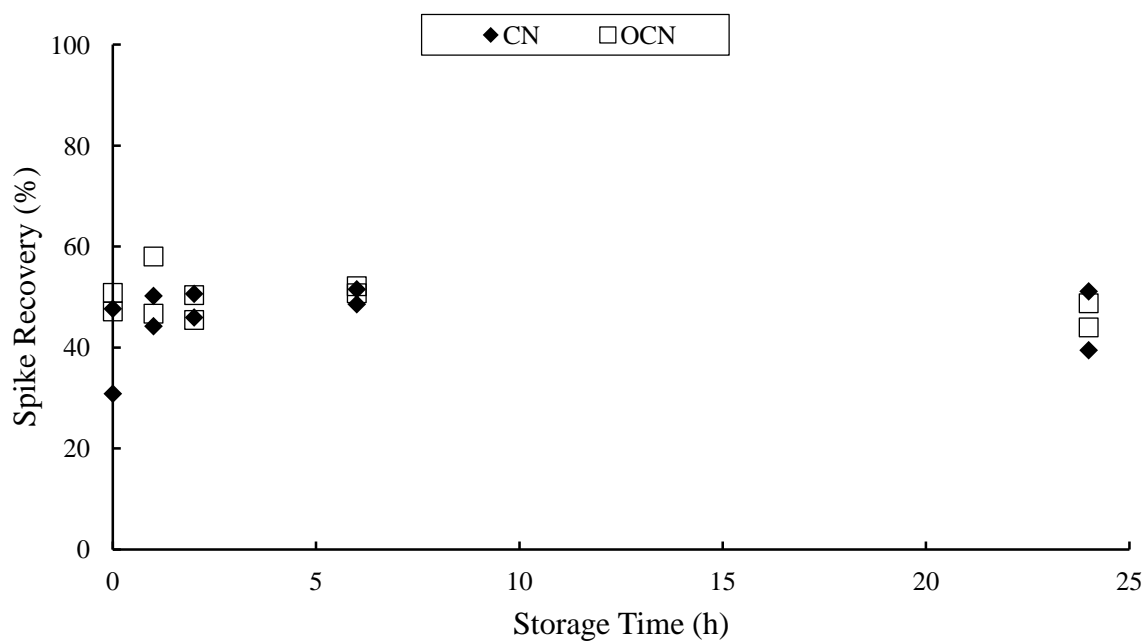
Figure 12. Storage stability of spiked surface coupons. Upper panel shows glazed ceramic tile and lower panel shows ton container section.

3.3.5   Transfer Efficiency from Coupons

        Transfer efficiency data were generated by spiking a mixed working solution of CN and OCN onto glazed ceramic tile, painted tile, and ton container sections. The spike solution was then allowed to age for 15 min before the coupons were wiped using the procedure described in Section 3.4.1 of this report. In this experiment, the coupons were sequentially wiped 10 times, and then each wipe was individually extracted and analyzed. The spiking solution was prepared in deionized water, and the nominal spike amount was 1.5 mg for both CN and OCN. In addition to the spiked coupons, one unspiked coupon of each type was processed to act as a matrix blank. Four LCS samples were prepared that consisted of the 10 µL of spiking solution added directly to 10 mL of extraction solution. The LCS samples were used to establish the theoretical spike level.

        Upon testing all 10 wipes, no CN or OCN was detected on any of the unspiked coupons. The average ($n = 30$) recovery for the CCV samples was 93.4% and ranged from 80.4 to 111%. The transfer efficiency data are illustrated in Figure 13. The overall average transfer efficiency of both CN and OCN from the glazed tile was 79.0%, with the majority (~72% of total) removed by the first wipe. There was no CN or OCN detected on wipes 4 through 10. The overall average transfer efficiency of both CN and OCN from the painted tile was 78.6%, with a significant amount (~37% of total) removed by the first wipe. CN and OCN were detected in wipes up through wipe 7. The overall average transfer efficiency of both CN and OCN from the ton container section was 9.41%, with each of the first three wipes removing ~30% of the total CN/OCN recovered. There were small amounts of CN and OCN recovered on wipes 4 and 5, and no detectable CN or OCN was recovered after wipe 5. The low transfer efficiency of free CN and OCN from the ton container section was likely due to complexation of free CN and OCN with iron contained in the ton container section.[27,28]
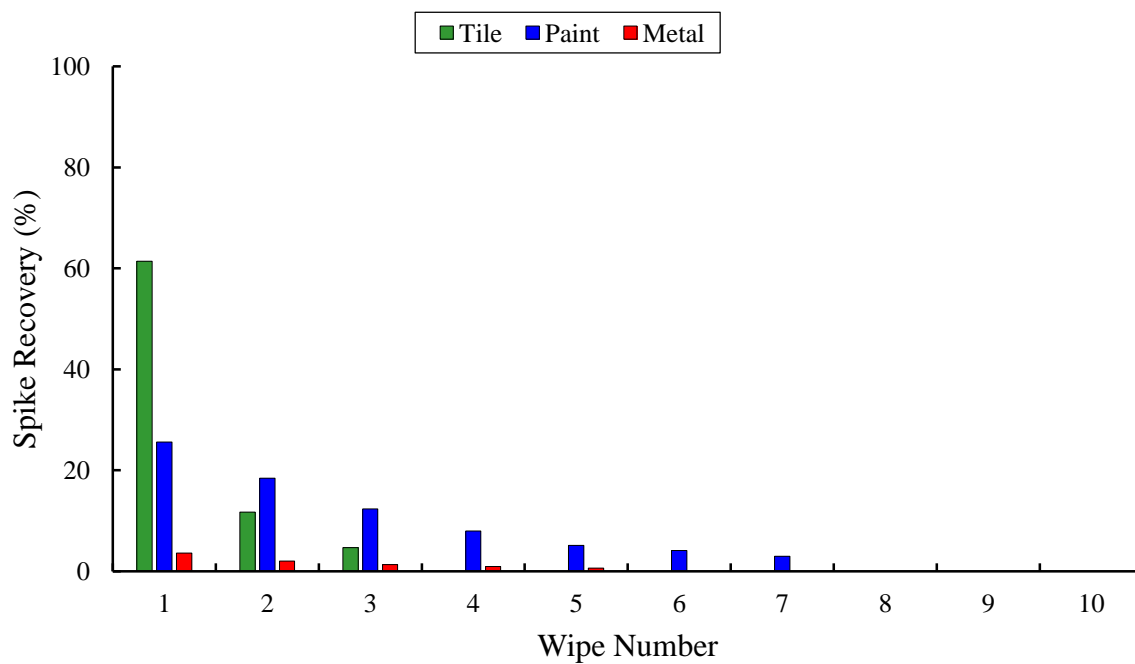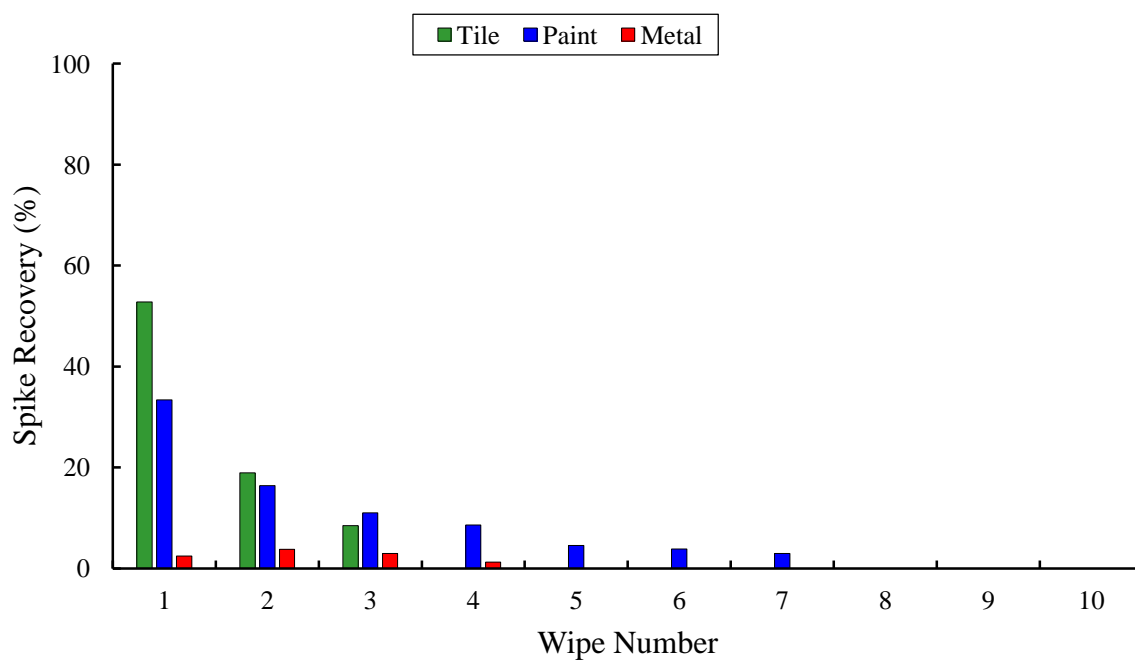
Figure 13. Transfer efficiency from surface coupons. Upper panel shows CN recovery and lower panel shows OCN recovery. Ten sequential wipes were conducted per coupon.

3.3.6   Estimation of Overall Detection Limits (ODLs)

          Precision and accuracy data were generated by spiking a mixed solution of CN and OCN onto glazed ceramic tiles. The spike solution was allowed to age for 15 min before the tile was wiped. The wipes were then extracted using the procedure outlined in Section 3.4 of this report. Spiking solutions were prepared in deionized water, and different concentration spiking solutions were prepared so the spike volume of 10 µL would be constant for all spike levels. Multiple replicates ($n = 10$) were independently prepared, extracted, and analyzed at four nominal spike levels ranging from 0.25 to 1 mg per wipe. In addition to the spiked tiles, three unspiked tiles were processed to act as matrix blanks. Three LCS samples were prepared for each spike level and consisted of 10 µL spiking solution added directly to 10 mL of extraction solution. The LCS samples were used to establish the theoretical spike level.

          In all cases, no CN or OCN was detected in any of the matrix blank samples ($n = 3$). The average ($n = 30$) recovery for the CCV samples was 92.1% and ranged from 81.4 to 109%. The precision and accuracy data are summarized in Table 3. The average recovery of CN across all spiking levels was 45.2%, with a 95% CI of 41.5 to 48.9%. The average recovery of OCN across all spiking levels was 45.6%, with a 95% CI of 42.1 to 49.1%. The overall spike recovery for both analytes was 45.4%, with a 95% CI of 42.9 to 47.9%. There was no significant difference in spike recovery as a function of spike amount, as illustrated in Figure 14. Using the regression function in Excel, the Student's t statistics were 0.1375 and –0.01863 for the slopes of the linear regression lines for CN and OCN, respectively. The critical value ($t_{0.05/2,38}$) of the Student's t statistic was between 2.02 and 2.04, so the critical value was not exceeded.[21] This demonstrated that the slopes of both linear regression lines were not significantly different from zero at the 95% confidence level. Evaluation of the precision and accuracy data indicated that the entire analytical process (collection, extraction, and analysis) was under control and suitable for quantitative analysis of residual CN and OCN from this surface.

          Using the precision data in Table 3 and the average LCS values, the ODLs were estimated using the approach outlined in Section 2.8 of this report. This estimation is illustrated in Figure 15. The ODLs were 0.13 and 0.10 mg per wipe for CN and OCN, respectively.

Table 3. Precision and Accuracy Data for Spike Recovery from Glazed Tile. Precision is the SSD of determined concentration. Accuracy is average ($n = 10$) percent recovery of spike relative to LCS value.

CN Spike Level[a] (mg)	Precision (mg)	Accuracy	
		(%)	95% CI[b]
0.235	0.0438	47.1	±13.3
0.470	0.0509	42.8	±7.75
0.678	0.0564	43.8	±5.95
1.04	0.0579	47.0	±3.98

a. Determined by analysis of triplicate LCS.
b. The 95% CI calculated by Excel 2007.

OCN Spike Level[a] (mg)	Precision (mg)	Accuracy	
		(%)	95% CI[b]
0.208	0.0375	47.5	±12.9
0.430	0.0405	42.2	±6.73
0.630	0.0491	46.5	±5.57
0.918	0.0514	46.0	±4.00

a. Determined by analysis of triplicate LCS.
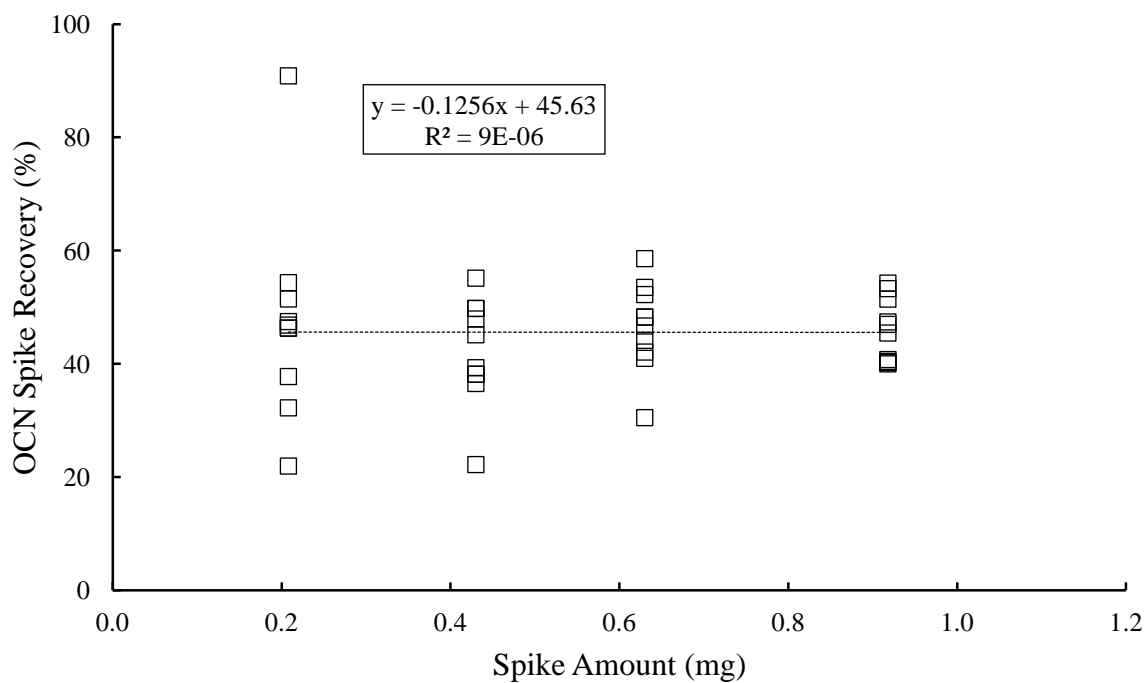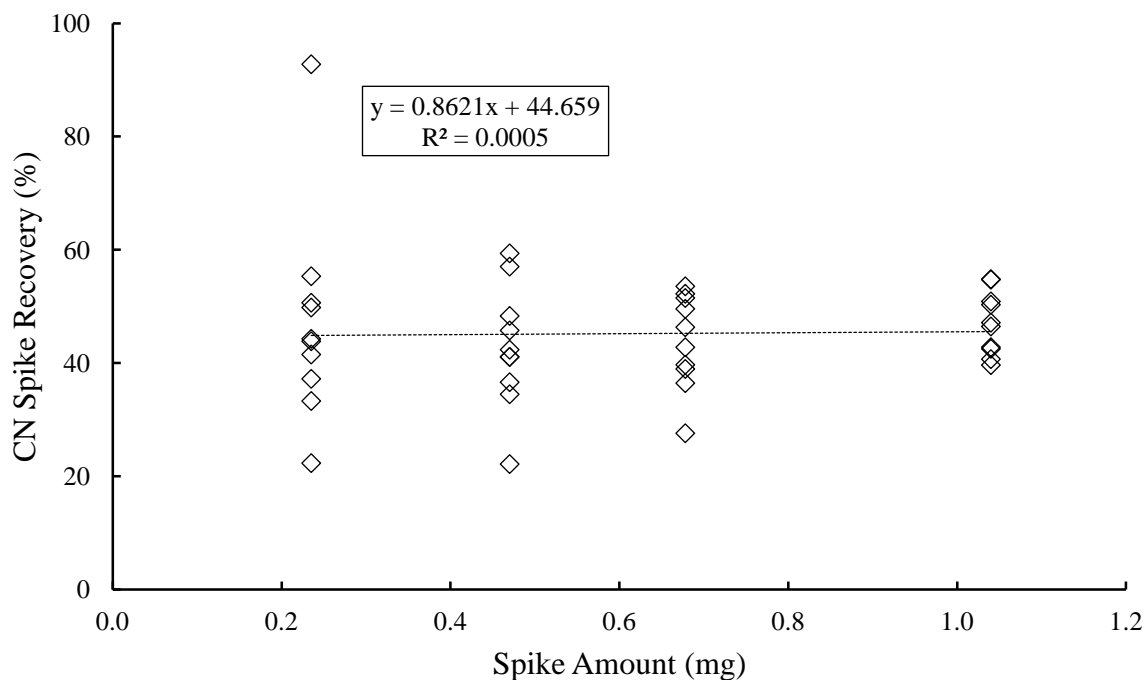b. The 95% CI calculated by Excel 2007.

Figure 14. Spike recovery as a function of spike amount from glazed tile. Upper panel shows CN recovery and lower panel shows OCN recovery. The slopes are not significantly different from zero at the 95% confidence level.
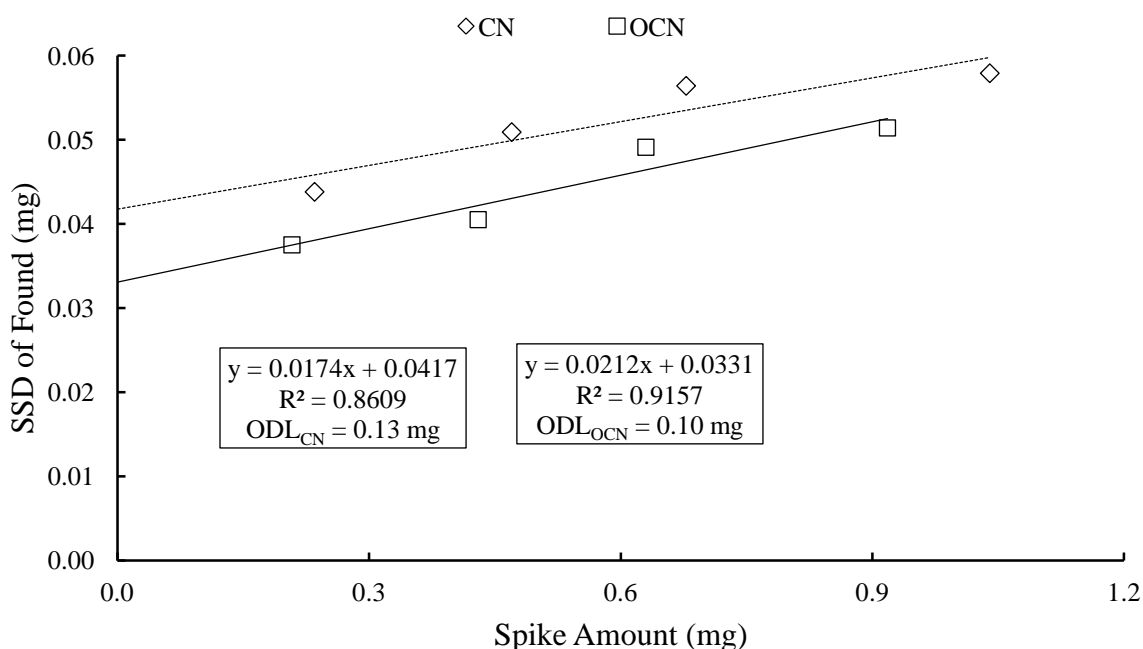
Figure 15. Estimation of the ODLs.

3.4 Validated Method Protocols

The CE analytical protocol is described in Section 2.6 of this report. The following sections describe the collection and extraction protocols used in the current laboratory study. Suggestions on implementing these protocols in the field are also included in this section of the report.

3.4.1 Collection Protocol

The wipes were 2×2 in. square gauze pads manufactured by Johnson and Johnson (part number 8137-008521, New Brunswick, NJ). The gauze pad material was a rayon/polyester/cellulose blend. The wipes were used as-received from the manufacturer, with no special cleaning of the wipe performed prior to sampling. The wipes were pre-moistened with 0.5 mL of deionized water just before use.

A 100 cm^2 (10×10 cm) sample area was used in all laboratory studies involving the ceramic tiles to support validation of this collection protocol. The wipe material was rubbed across the tile sample area using a serpentine pattern, first moving the wipe from left to right then up and down. Two passes were made on each axis, and the wipe material was folded in on itself after each pass. A pair of single-use plastic forceps was used to rub the wipe across the tile surface. The wipe was then placed into the 40 mL vial that was used during the extraction protocol. The protocol for the ton container section was different because the coupon was smaller than the tile. The entire surface of the ton container coupon was rubbed using a back-and-forth motion in the same axis.

In actual operations, it will be important to apply consistent pressure with the wipe and sample approximately the same area each time. Using a gloved hand will be the easiest way to achieve consistent pressure, but the gloves should be changed between wipe samples to prevent cross-contamination. The use of a sampling template to consistently sample the same area each time is recommended. In addition, during actual operations, multiple (at least two) wipes should be collected from the same area, and the wipe sample should be placed into a 40 mL vial containing the 10 mL of extraction solution. To minimize leaks and evaporative losses, the threads of the vial should be wrapped with Teflon tape.

3.4.2   Extraction Protocol

Extraction of the compounds from the wipe was accomplished by adding 10 mL of extraction solution to the 40 mL vial, then capping and placing the vial in the sonicator bath for 60 min. Ice was kept in the water bath to prevent the samples from getting too hot. Once the sonication was complete, a sample of the extraction solution (~2 mL) was removed and pressure-filtered through a 0.2 µm nylon Acrodisc filter. This filtrate was transferred to a 4 mL amber glass vial and stored at ~4 °C until analyzed using the CE protocol described in Section 2.6 of this report.

In actual operations, it is recommended that wipes also be analyzed by the total cyanide method[26] because most of the free CN and OCN will have complexed with the metals associated with the EDS.

4.   CONCLUSIONS

A surface wipe method for free CN and OCN was successfully validated using collection protocols suitable for personnel wearing PPE in a contaminated environment. There were no significant differences in method performance for free CN or OCN. Under the conditions evaluated during the current laboratory study, the overall average accuracy (spike recovery) from the wipe material was 76.7%, with a 95% CI of 75.7 to 77.6%, and the overall average accuracy (spike recovery) using a single wipe from an impervious surface was 45.4%, with a 95% CI of 42.9 to 47.9%. The ODLs for the entire process were estimated to be 0.13 mg CN and 0.10 mg OCN per wipe. The validation data collected during this study indicated that the entire analytical process (collection, extraction, and analysis) was under control and suitable for quantitative analysis of free CN and OCN from impervious surfaces.

During the course of this study, it was concluded that a significant portion of the free CN and OCN can become unavailable for extraction, and will not be detected by the CE analysis protocol. The most likely cause of this problem is the complexation of free CN and OCN with metals, such as iron and copper.[27,28] It was demonstrated during this study that an alternative method, the total cyanide method,[26] would quantitatively recover the CN and OCN spiked onto the wipe. It is recommended that both free and total methods be applied during efforts to evaluate equipment used during EDS operations.

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ACRONYMS AND ABBREVIATIONS

AC   hydrogen cyanide

APG   Aberdeen Proving Ground

CAS   Chemical Abstract Service

CCV   continuing calibration verification

CE   capillary electrophoresis

CK   cyanogen chloride

CI   confidence interval

ClCN   cyanogen chloride

CN   free cyanide ion

CWA   chemical warfare agents

CWM   chemical warfare materiel

CZE   capillary zone electrophoresis

DL   detection limit

DoD   Department of Defense

EDL   extraction detection limit

EDS   Explosive Destruction System

EPA   Environmental Protection Agency

HCN   hydrogen cyanide

IDL   instrument detection limit

LCS   laboratory control spike

MDL   method detection limit

NSCM   non-stockpile chemical materiel

OCN   free cyanate ion

ODL   overall detection limit

PMNSCM   Product Manager for Non-Stockpile Chemical Materiel

PPE   personal protective equipment

RCWM   recovered chemical warfare materiel

SSD   sample standard deviation

TIC   toxic industrial chemical

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